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Crystal Structure of Barium Titanyl Oxalate $BaTiO(C_2O_4)_2 \cdot 4.5H_2O$

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The hydrated phase of barium titanyl oxalate, $BaTiO(C_2O_4)_2 \cdot 4.5\,H_2O$, is monoclinic with $a = 13.382(2)$, $b = 13.812(2)$, $c = 14.044(2)$ Å, $\beta = 91.48(1)°$, space group $P2_1/n$, $Z = 8$. The structure has been determined from Patterson and Fourier syntheses. The refinement was done by the method of least-squares. The final R values were $R = 0.056$ and $R_w = 0.079$ for 3261 unique reflections. The structure is characterized by a body-centered arrangement of finite groups consisting of four vertex-sharing TiO_6 distorted octahedra. These groups are connected by barium polyhedra and oxalate groups. The study shows that the water molecule number is 4.5 by formula rather than 4 reported previously. This conclusion is supported by TG measurements.

Introduction

The preparation of the hydrated phase of barium titanyl oxalate (BTO) for conversion by pyrolysis to stoichiometric barium titanate of high purity was described long ago (*1*). The composition reported for this material, in which the molar ratio of TiO_2 to BaO is unity, is $BaTiO(C_2O_4)_2 \cdot 4H_2O$. The scheme of its thermal decomposition has been investigated by several authors (*2, 3*). The stoichiometry and nature of this important precursor of barium titanate ceramics has been studied extensively and discussed in terms of factors influencing its synthesis (*3*). Although the powder diffraction pattern was described as "complicated" (*3, 4*), a sample of BTO was recently investigated by means of high resolution conventional X-ray powder diffraction, using strictly monochromatic radiation (*5*). The indexing of the powder data was carried out by means of the successive dichotomy method (*6, 7*) and a monoclinic cell with high figures of merit [$M_{20} = 46, F_{30} = 107(0.0056, 50)$] was found. The large unit cell (2594.9 Å^3) explains the high density of diffraction lines in the powder pattern and indexing confirms that BTO is a single phase. Moreover, in this work the average of the FWHM values of diffraction lines (0.07° 2θ), in the observed angular range, was comparable to the instrumental resolution function (*8*), which is an indication that structural imperfections are negligible and that coherently diffracting domains have large dimensions. We were motivated by these features to make a careful observation, by optical microscopy, of several samples of BTO, from which a small single crystal could be isolated. The present paper describes the determination of the crystal structure of the hydrated phase of barium titanyl oxalate and, as a consequence of the results obtained,

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the initial stages of its thermal decomposition was again investigated and is also reported.

Experimental Considerations

The double oxalate of barium and titanium was obtained by the method described in Ref. (*1*), using $BaCl_2 \cdot 2H_2O$, $TiCl_4$, and $H_2C_2O_4 \cdot 2H_2O$ (Merck pro analysi) as starting materials. The TG analysis was carried out with a Rigaku Thermoflex TG-DSC. Powder samples of about 25 mg were spread evenly, in a platinum sample holder. The samples were heated in air with a slow heating rate of 10°C hr^{-1} in the range 18–800°C.

Structure Determination and Refinement

A small crystal (0.22 × 0.24 × 0.17 mm) was selected from the powder and mounted on an Enraf–Nonius CAD4 diffractometer, with graphite-monochromated Mo$K\alpha$ radiation. Systematic absences ($h0l: h + l$ odd; $0k0: k$ odd) are consistent with the monoclinic $P2_1/n$ space group. Cell constants, determined by the least-squares treatment of 25 reflections with 2θ values between 17.5 and 21.8°, are in agreement with the solution derived from the automatic indexing of the powder diffraction pattern (*7*). One set of intensities ($h: 0 \rightarrow 15, k: 0 \rightarrow 15, l: \overline{15} \rightarrow 15$) was collected at room temperature by the θ–2θ scanning technique to give 3936 unique reflections with $\sin(\theta)/\lambda \leq 0.565 \text{Å}^{-1}$. Within this set, 3261 reflections were considered as observed by means of the criterion $I > \sigma(I)$. The standard reflections ($\bar{1}70$, 315, 305) showed no significant variation during the data collection. Data were corrected for Lorentz and polarization effects. Due to the small size of the crystal no absorption correction was applied. Atomic scattering factors were taken from "International Tables for X-ray Crystallography" (*9*). All calculations were performed with a MICROVAX 3100 computer by means of the SDP programs (*10*).

TABLE I

CRYSTALLOGRAPHIC DATA FOR $BaTiO(C_2O_4)_2 \cdot 4.5\ H_2O$

Empirical formula	$Ba_1Ti_1C_4O_{13.5}H_9$
Formula weight	458.27
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	13.382(2)
b(Å)	13.812(2)
c(Å)	14.044(2)
β(°)	91.48(1)
V(Å^3)	2594.9
Z	8
D_{calc} (g · cm^{-3})	2.34
D_{obs} (g · cm^{-3}) [5]	2.27
F_{000}	1712
Radiation (Å)	$\lambda = 0.71069$
Data collection	$h, k, \pm l$
No. observations	3261
No. variables	355
R	0.056
R_w	0.079

The structure was solved by the heavy atom method which yielded the positions of both independent Ba atoms. The positions of the remaining atoms were obtained from two successive Fourier maps. At this stage, the 37 independent nonhydrogen atoms correspond to the formula $BaTiO(C_2O_4)_2 \cdot 3.5\ H_2O$. No subsequent peaks with suitable distances from Ba or Ti atoms were found. The R and R_w values ($w^{-1} = \sigma^2(F) + (0.04\ |\ F_o\ |\ )^2$), including anisotropic thermal parameters, were 6.9 and 10.2, respectively. The final Fourier-difference map showed two additional peaks with a height of 5.1 and 4.2 e/Å^3. These peaks are not bonded to Ba and Ti atoms and could correspond to one additional water molecule, leading to the formula $BaTiO(C_2O_4)_2 \cdot 4.5H_2O$. They were included in final cycles of the least-squares refinement and refined anisotropically. The R and R_w values then decreased to 5.6 and 7.9, respectively. The refinement of occupation numbers for these two peaks gave the values 0.94 and 0.69, but did not improve the R-factors, which

TABLE II

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B_{eq}(Å^2)
Ba1	0.53500(5)	0.33772(5)	0.45467(4)	1.87(1)
Ba2	0.46724(5)	0.06919(6)	0.26211(5)	2.62(1)
Ti1	0.1277(1)	0.1226(2)	0.5274(1)	1.72(4)
Ti2	0.4182(1)	0.3890(1)	0.8827(1)	1.69(4)
C1	0.0480(8)	0.1828(8)	0.7043(8)	2.0(2)
C2	0.1548(8)	0.1495(8)	0.7319(8)	2.0(2)
C3	0.3185(8)	0.1763(9)	0.4548(8)	2.3(2)
C4	0.2754(9)	0.2715(8)	0.4887(8)	2.6(2)
C5	0.4619(8)	0.3158(8)	0.6952(8)	2.2(2)
C6	0.9696(8)	0.0745(8)	0.1871(7)	1.9(2)
C7	0.2059(8)	0.3477(8)	0.8906(8)	2.1(2)
C8	0.2592(8)	0.2894(9)	0.9717(8)	2.2(2)
O1	0.4901(6)	0.2886(6)	0.2646(5)	2.7(2)
O2	0.0269(5)	0.1750(6)	0.6159(5)	2.2(2)
O3	0.2071(5)	0.1273(6)	0.6599(5)	2.1(2)
O4	0.6831(6)	0.3520(6)	0.3165(5)	2.7(2)
O5	0.4004(6)	0.1733(6)	0.4210(6)	2.8(2)
O6	0.2586(5)	0.1027(5)	0.4650(5)	2.1(2)
O7	0.3259(7)	0.3453(6)	0.4821(7)	3.6(2)
O8	0.1861(5)	0.2656(6)	0.5182(5)	2.4(2)
O9	0.4871(7)	0.2632(6)	0.6292(5)	3.7(2)
O10	0.4322(6)	0.2864(6)	0.7771(5)	2.3(2)
O11	0.4868(6)	0.4651(6)	0.6135(5)	2.7(2)
O12	0.4511(6)	0.4678(6)	0.7667(5)	2.2(2)
O13	0.2655(6)	0.3905(6)	0.8363(5)	2.4(2)
O14	0.6147(6)	0.1514(6)	0.3866(6)	2.8(2)
O15	0.3559(6)	0.2941(6)	0.9685(5)	2.4(2)
O16	0.7115(6)	0.2562(6)	0.5289(6)	2.9(2)
O17	0.3937(5)	0.4955(6)	0.9524(5)	2.1(2)
O18	0.0432(5)	0.1399(6)	0.4269(5)	1.9(1)
Ow1	0.2548(9)	0.085(1)	0.2225(9)	6.7(3)
Ow2	0.6474(7)	0.1074(8)	0.1704(7)	4.3(2)
Ow3	0.4266(2)	−0.092(1)	0.150(1)	12.1(6)
Ow4	0.5923(8)	−0.0716(8)	0.320(1)	8.0(4)
Ow5	0.439(1)	0.1311(9)	0.0759(9)	6.7(3)
Ow6	0.6993(9)	0.4578(8)	0.5234(9)	5.9(3)
Ow7	0.388(1)	−0.065(1)	0.385(1)	11.0(4)
Ow8	0.325(1)	0.428(1)	0.172(1)	8.5(4)
Ow9	0.366(2)	0.076(2)	0.908(1)	11.8(6)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}* [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos\gamma)*B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

TABLE III

Bond Distances (Å) with Their Estimated Standard Deviations

Ba1	O1	2.806(4)	Ba2	Ow5	2.771(7)	C7	C8	1.555(9)
Ba1	O4	2.825(5)	Ba2	Ow7	2.800(8)	C1	O1^{iii}	1.231(8)
Ba1	O5	2.934(5)	Ti1	O2	2.000(4)	C1	O2	1.272(8)
Ba1	O7	2.842(5)	Ti1	O3	2.119(4)	C2	O3	1.285(7)
Ba1	O9	2.755(5)	Ti1	O6	2.003(4)	C2	O4^{iii}	1.239(8)
Ba1	O11	2.933(5)	Ti1	O8	2.135(5)	C3	O5	1.209(8)
Ba1	O11^{iv}	2.905(5)	Ti1	O17^{i}	1.808(5)	C3	O6	1.308(8)
Ba1	O14	2.962(5)	Ti1	O18	1.800(4)	C4	O7	1.232(8)
Ba1	O16	2.796(5)	Ti2	O10	2.068(4)	C4	O8	1.279(8)
Ba1	Ow6	2.903(6)	Ti2	O12	2.021(4)	C5	O9	1.233(8)
Ba2	O1	3.054(5)	Ti2	O13	2.130(4)	C5	O10	1.295(8)
Ba2	O5	2.827(5)	Ti2	O15	1.985(5)	C6	O11	1.200(8)
Ba2	O14	2.840(5)	Ti2	O17	1.807(4)	C6	O12	1.294(8)
Ba2	Ow1	2.894(7)	Ti2	O18^{ii}	1.814(4)	C7	O13	1.268(8)
Ba2	Ow2	2.820(6)	C1	C2	1.543(9)	C7	O14^{iii}	1.222(8)
Ba2	Ow3	2.788(9)	C3	C4	1.52(1)	C8	O15	1.300(8)
Ba2	Ow4	2.681(6)	C5	C6	1.528(9)	C8	O16^{iii}	1.217(8)

Note. i: $1/2 - x, y - 1/2, 1.5 - z$; ii: $1/2 + x, 1/2 - y, 1/2 + z$; iii: $x - 1/2, 1/2 - y, 1/2 + z$; iv: $1 - x, 1 - y, 1 - z$.

suggests that the chemical interpretation of this attempt is not obvious. Crystallographic data and final atomic parameters with equivalent temperature factors are given in Tables I and II, respectively. In Table II, O1–O16 correspond to the oxygen atoms of oxalate groups, O17 and O18 to the O^{2-} ions of TiO groups, Ow1–Ow7 to the water molecules and Ow8 and Ow9 to the additional nonbonded water molecules. Selected bond dis-

TABLE IV

Bond Angles (°) with Their Estimated Standard Deviations

O2	Ti1	O3	76.9(2)	O10	Ti2	O17	166.6(2)	C4	C3	O5	120.7(6)
O2	Ti1	O6	159.9(2)	O10	Ti2	O18	89.6(2)	C4	C3	O6	113.6(6)
O2	Ti1	O8	87.5(2)	O12	Ti2	O13	88.7(2)	O5	C3	O6	125.7(7)
O2	Ti1	O17	98.2(2)	O12	Ti2	O15	162.4(2)	C3	C4	O7	118.8(6)
O2	Ti1	O18	91.1(2)	O12	Ti2	O17	92.6(2)	C3	C4	O8	114.5(6)
O3	Ti1	O6	88.1(2)	O12	Ti2	O18	100.1(2)	O7	C4	O8	126.7(7)
O3	Ti1	O8	81.3(2)	O13	Ti2	O15	77.0(2)	C6	C5	O9	120.6(6)
O3	Ti1	O17	88.4(2)	O13	Ti2	O17	88.3(2)	C6	C5	O10	113.7(6)
O3	Ti1	O18	166.8(2)	O13	Ti2	O18	167.5(2)	O9	C5	O10	125.6(6)
O6	Ti1	O8	76.9(2)	O15	Ti2	O17	97.1(2)	C5	C6	O11	122.3(6)
O6	Ti1	O17	94.6(2)	O15	Ti2	O18	92.6(2)	C5	C6	O12	111.8(5)
O6	Ti1	O18	102.3(2)	O17	Ti2	O18	100.0(2)	O11	C6	O12	125.9(6)
O8	Ti1	O17	166.8(2)	C2	C1	O1	121.5(6)	C8	C7	O13	113.6(5)
O8	Ti1	O18	93.0(2)	C2	C1	O2	113.5(5)	C8	C7	O14	118.4(6)
O17	Ti1	O18	98.8(2)	O1	C1	O2	125.0(6)	O13	C7	O14	128.0(6)
O10	Ti2	O12	76.4(2)	C1	C2	O3	113.4(5)	C7	C8	O15	112.6(6)
O10	Ti2	O13	83.9(2)	C1	C2	O4	120.2(6)	C7	C8	O16	121.0(6)
O10	Ti2	O15	91.7(2)	O3	C2	O4	126.5(6)	O15	C8	O16	126.4(6)

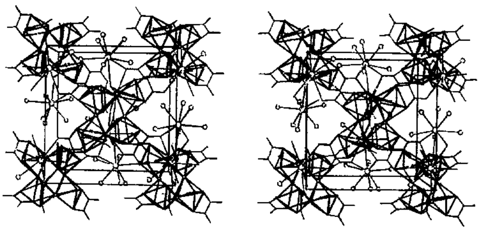

FIG. 1. Stereoscopic view of the unit cell of $BaTiO(C_2O_4)_2 \cdot 4.5H_2O$ along *c*, with *a* horizontal and *b* vertical.

tances and angles are listed in Tables III and IV.

Results and Discussion

A stereoscopic view of the structure is shown in Fig. 1, from which its three-dimensional nature is readily apparent. Figure 2 shows different parts of the structure. Ba1 (Fig. 2a) is bonded to 10 oxygen atoms arising from five C_2O_4 groups and one water molecule. The Ba1–O distances are in the range 2.755 to 2.962 Å (mean value: 2.866 Å). Ba2 (Fig. 2b) is bonded to 9 oxygen atoms due to three C_2O_4 groups and six water molecules with bond lengths ranging from 2.681 to 3.054 Å (mean value: 2.830 Å). The two Ti atoms are octahedrally bonded to two O^{2-} ions and two C_2O_4 groups (Fig. 2c). This coordination number of 6 for Ti with O or oxygen-containing ligands is the one most frequently encountered. The Ti–O distances are in the range 1.800 to 2.135 Å. The values of the Ba–O and Ti–O distances and the characteristics of the $C_2O_4^{2-}$ groups are in good agreement with those reported in the literature (*11–15*). It can be noted that the distances Ti–O^{2-} (mean value: 1.807(4) Å) are significantly shorter than the distances between Ti and the oxygen atoms of the oxalate groups (mean value: 2.058(4) Å). The four independent oxalate groups have the same coordination. Figure 2d shows the environment of the oxalate group, which acts as a bidentate ligand to Ba1 and Ti and as a monodentate ligand to Ba2. Each water molecule, except Ow8 and Ow9, is bonded to one Ba atom. Although attempts to locate H atoms failed, no ambiguity exists for differentiating O^{2-} and water molecules. Moreover, according to Baur's criteria (*16*), the possible hydrogen bonds are listed in Table V, where O–O distances less than 3.10 Å are listed as well as the corresponding angles which are within acceptable limits when compared to the tetrahedral angles.

A way of looking at the crystal structure is to regard it as a body-centered arrangement of finite Ti_4O_{20} groups consisting of four vertex-sharing TiO_6 distorted octahedra (Fig. 2e). The shared vertices are O17 or O18. As shown in Fig. 1, these groups are connected by oxalate ions and Ba2 polyhedra along the [100] and [010] directions and by oxalate ions and Ba1 polyhedra along the [001] and [110] directions. This description, corresponding to the formula $BaTiO(C_2O_4)_2 \cdot 3.5H_2O$, does not include the two last oxygen atoms (Ow8–Ow9 in Table II). These atoms, which correspond to one water molecule by chemical formula, are not bonded to the heavy atoms and are located in the vicinity of the Ba polyhedra. (The shortest distances to barium atoms are Ba1–Ow9 = 4.66 Å, Ba2–Ow8 = 4.50 Å, and Ba2–Ow9 = 3.88Å.) Their distances from the nearest oxygen atoms and oxalate groups are consistent with hydrogen bonds (Table V). By including these oxygen atoms, structural analysis indicates that the composition of BTO has to be written $BaTiO(C_2O_4)_2 \cdot (3.5 + 1)H_2O$, while in previous studies, based on TG measurements, a tetrahydrate was generally reported (*2, 3*). In the TG analysis described by Gallagher and Schrey (*2*), the curve obtained at a heating rate of 60°C hr^{-1} revealed that the mass loss begins at the outset of the heating and no frank plateau is observed, making it difficult to evaluate the precise number of water molecules in the material. Due to the detection of

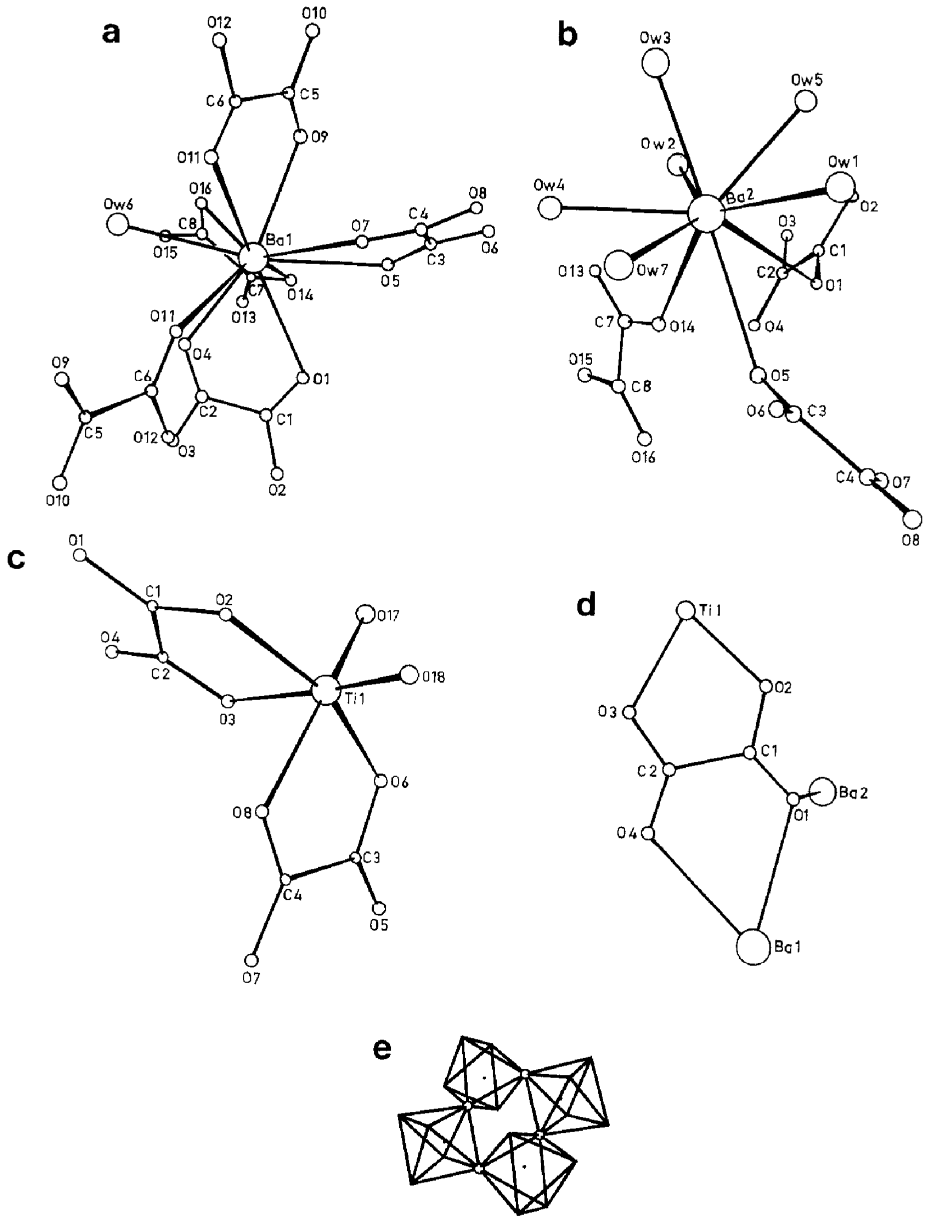

FIG. 2. The environment of Ba1 (a), Ba2 (b), Ti (c), and oxalate group (d); (e) represents the Ti_4O_{20} group of four vertex-sharing octahedra.

TABLE V

Possible Hydrogen Bonds

Distances (Å)		Angles (°)	
Ow1–Ow6	2.893(7)	Ow6–Ow1–Ow8	104.7(3)
–Ow8	2.871(10)		
Ow2–O8	2.821(6)	O8–Ow2–O13	121.0(3)
–O13	2.775(7)	O8–Ow2–Ow9	105.8(3)
–Ow9	2.762(12)	O13–Ow2–Ow9	112.1(3)
Ow3–Ow9	2.943(17)		
Ow4–O9	2.955(8)	O3–Ow4–O9	94.7(2)
–O3	2.795(7)		
Ow5–O2	2.775(7)	Ow1–Ow8–Ow7	74.9(3)
Ow6–O7	2.900(6)	Ow2–Ow9–Ow3	90.5(4)
		Ow2–Ow9–Ow5	130.2(5)
Ow7–Ow8	2.867(13)	Ow2–Ow9–O4	95.6(3)
		Ow3–Ow9–Ow5	83.4(5)
Ow9–Ow5	2.632(11)	Ow3–Ow9–O4	129.4(5)
–O4	2.910(11)	Ow5–Ow9–O4	125.8(4)

two kinds of water molecule in the course of the structure determination, a TG analysis was carried out in air at a low heating rate (10°C hr^{-1}) to give a better resolution. The TG curve shown in Fig. 3 is similar to the result given by Gallagher and Schrey (*2*), except in the initial stages. Indeed, a slight inflection point is observed at 60°C for a value of $\Delta m/m_0$ close to 3.7%, which is consistent with a loss of one water molecule (3.93%). It could correspond to the loss of the water not coordinated to heavy atoms. The second inflection point, located approximately at 200°C, corresponds to a mass loss of 17.40% which is in good agreement with the total loss of water. (Theoretical value for 4.5 H_2O content is 17.68%.) In this second stage, the remaining 3.5 water molecules are eliminated from the precursor. Finally, the observed total mass loss is 49.00%, which corresponds to the formation of barium titanate (theoretical value 49.10%). The results of this TG study are in agreement with the chemical formula deduced from the structure analysis. Furthermore, samples of partially and completely dehydrated BTO, corresponding to 3.5, 1.0, 0.3, and 0.0 H_2O, respectively, were studied by powder diffraction. The results obtained show that the intensities of the diffraction lines decrease with decreasing water molecule content, yielding the anhydrous compound which is very poorly crystallized. This analysis suggests that no intermediate chemically defined phase exists and that the poorly crystalline feature of the anhydrous phase which is obtained can be due to the six water molecules removed from the polyhedra of the Ba2 atom in the course of the thermal decomposition.

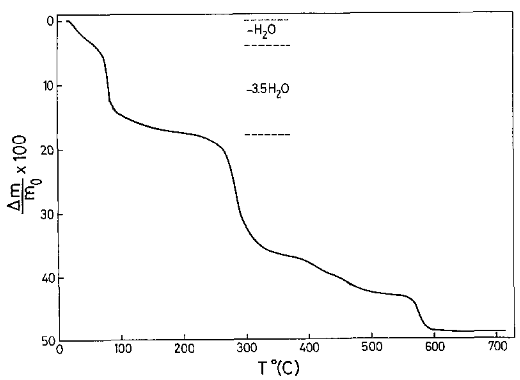

Fig. 3. Thermogravimetric curve (heating rate: 10°C · h^{-1}).

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